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Preparation and characteristics of an environmentally friendly hyperbranched flame retardant polyurethane hybrid containing nitrogen, phosphorus, and silicon

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Abstract

The NCO functional group of 3-isocyanatoproply triethoxysilane (IPTS) and the OH functional group of DOPO-BQ were used to conduct an addition reaction. Following completion of the reaction, triglycidyl isocyanurate (TGIC) was introduced to conduct a ring-opening reaction. Subsequently, a sol-gel method was used to take place a hydrolysis-condensation reaction on TGIC-IPTS-DOPO-BQ to form a hyperbranched nitrogen–phosphorous–silicon (HBNPSi) flame retardant. This flame retardant was incorporated into a polyurethane (PU) matrix to prepare a hybrid material. Fourier-transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), limiting oxygen index (LOI), UV-VIS spectrophotometry, and Raman analysis were conducted to structure characterization and analyzed transparency, thermal stability, flame retardancy, and residual char to understand the flame retardant mechanism of prepared hybrid materials. After the flame retardant was added, the maximum degradation rate decreased from −36 wt%/min to −17 wt%/min, the integral procedure decomposition temperature (IPDT) increased from 348 ℃ to 488 ℃, and the char yield increased from 0.7 to 8.1 wt%. The aforementioned results verified that thermal stability of PU can be improved after adding HBNPSi. The LOI analysis indicated that the pristine PU was flammable because the LOI of pristine PU was only 19. When the content of added HBNPSi was 40%, the LOI value was 26; thus the PU hybrid became nonflammable.

Keywords：polyurethane, sol-gel method, hyperbranched hybrid, thermal stability, flame retardant

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1. Introduction

A reaction of isocyanate and polyhydric alcohol can form polyurethane (PU). It is one kind of polymer with high crosslinking and specific characteristics that are suitable for various types of materials [1], such as household mattresses, furniture, sealants, adhesives, leather, and various types of biomedical products [2]. However, PU is highly flammable because it contains considerable amounts of aliphatic segments. Mechanical properties of PU deteriorate rapidly if the temperature exceeds 80 to 90 ℃ and serious thermal degradation occurs if the temperature exceeds 200 ℃; its application in many fields is greatly limited. Therefore, application of effective and environmentally friendly flame retardants in PU is crucial [3-7].

Halogen-free flame retardants are currently receiving increasing attention; the compounds that include phosphorus, nitrogen, and silicon are gradually replacing halogen flame retardants. A phosphorus-based flame retardant has two noteworthy characteristics. First, it can be volatilized to form phosphorus free radicals in a gas phase, which can capture free radicals produced from the materials in the fire. Second, phosphate flame retardants can catalyze char formation. Both of these characteristics of phosphorus flame retardants can stop combustion [7]. Additionally, with Si-O bonds as the main chain, siloxane has relatively high bond energy, and marked flexibility of Si-O chain segments, which contribute to excellent thermal stability under high temperatures [8].

The PU used in this study has several desirable characteristics, but all PUs have several shortcomings such as flammability, low melting point, and low heat tolerance. Therefore, the sol-gel method was used to prepare a flame retardant that contained nitrogen, phosphorus, and silicon, and combined it with PU to form a hybrid material. Additionally, Fourier-transform infrared spectroscopy (FT-IR) was used to conduct structure characterization. The thermostability of this hybrid material was measured through thermogravimetric analysis (TGA), integral procedural decomposition temperature (IPDT), and TGΔ. The flame retardancy of the hybrid material was determined through the limiting oxygen index (LOI). A Raman spectrum was used to study the mechanism of flame retardant from char analysis.

2. Experimental

2.1 Materials

Isophorone diisocyanate (IPDI) and dibutyltin dilaurate (DBTDL) were purchased from Alfa

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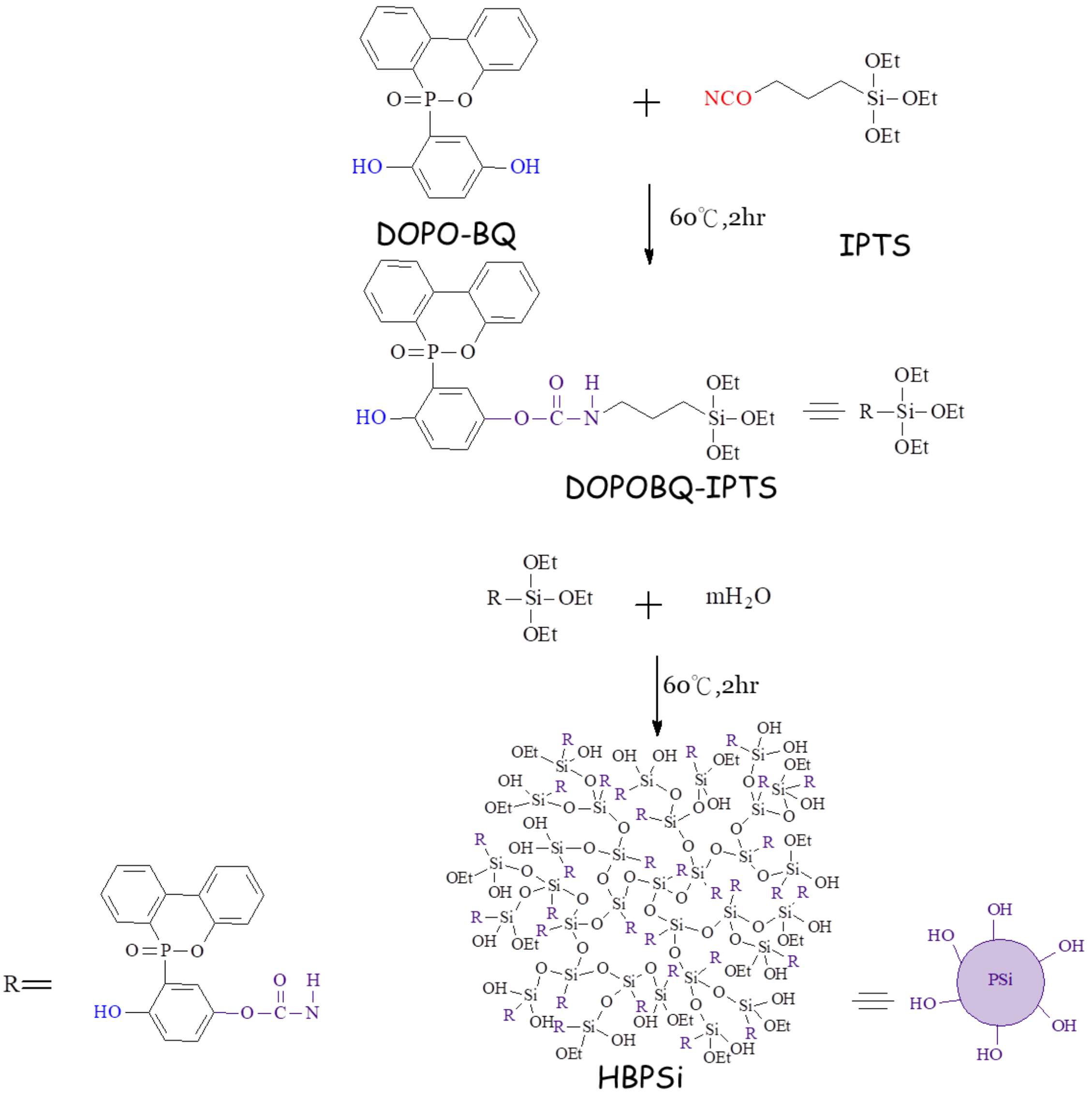
Aesar CO., Shore Road, Heysham, LA3 2XY, England. ARCOL POLYOL 1021(Polyol) was purchased from Bayer Material Science Taiwan Limited. 1, 4-butanediol (1, 4-BD), was purchased from Acros Chemical Co, New Jersey, USA. 3-Isocyanatopropyltriethoxysilane （IPTS）was purchased from GELEST, Inc., 11 steel Rd. EAST, Morrisville, PA, USA. Triglycidyl isocyanurate(TGIC) was purchased from TCI, Tokyo, Japan. 10-(2,5-Dihydroxyphenyl)-10H-9-oxa-10-phospha-phenantbrene-10-oxide (DOPO-BQ) was purchased from Sigma-Aldrich Co Ltd, Taipei, Taiwan. Anhydrous stabilized tetrahydrofuran (THF) was obtained from Lancaster Co., Morecambe, Lancashire, U.K. Hydrogen chloride (HCl) was purchased from ECHO Chemical Co., LTD, Taiwan.

2.2 Preparation of DOPOBQ-IPTS-TGIC

First, DOPO-BQ (7.58 g) and IPTS (5.78 g) were added into a 100 mL serum bottle, and then added 80 mL of THF solvent and 0.2 g of metal catalyst DBTDL. The aforementioned substances were stirred at 60 ℃ and allowed the substances to react for 2 hours. Subsequently, we added 0.72 mL of DI water into THF, instilled HCI, and adjusted the pH value to 4; the product of the sol-gel reaction was HBPSi. Additionally, TGIC (6.95 g) was dissolved in THF and conducted a sol-gel reaction for 2 hours on HBPSi. After the temperature reached 60 ℃, TGIC was slowly added into HBPSi, and allowed them to react at 60 ℃ for 2 hours. This formed a hyperbranched nitrogen–phosphorous–silicon (HBNPSi) flame retardant; its reaction is presented in Scheme 1.


DOPO-BQ
O=P–O
HO
OH
+
NCO
Si–OEt
OEt
60℃,2hr
IPTS
DOPOBQ-IPTS
O H
O–C–N
R–Si–OEt
+
mH2O
60℃,2hr
HBPSi
R=
PSi
HO
OH

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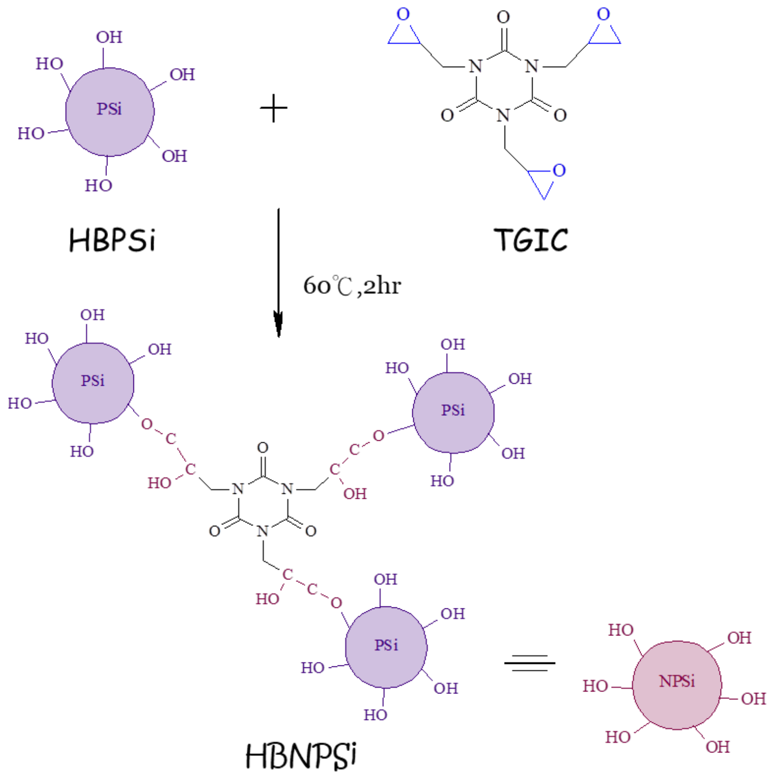

Scheme 1 the reaction of HBNPSi.

2.3 Preparation of PU/HBNPSi hybrid

IPDI (9.88 g) and Polyol (20 g) were added into a four-necked bottle in a nitrogen environment; the mixture was stirred by a magnetic stirrer at 60 ℃. Subsequently, DBTDL catalyst (0.3 g) was added into the four-necked bottle for a simultaneous reaction to form prepolymer. Following 2 hours of reaction, HBNPSi was slowly dripped into the four-necked bottle. After 2 hours of reaction, 1- 4 BD (0.8 g) was also allowed to react for 2 hours and observed whether viscosity increased. After viscosity increased for any sample, that sample was poured into a polytetrafluoroethylene mold and placed it into a vacuum oven for 24 hours of deaeration. After the temperature reached 60 ℃, it was placed in another circulating oven for 24 hours. When the temperature reached 60 ℃, the finished product was withdrawn and stored at room temperature for cooldown, thereby completing preparation of PU/HBNPSi. Its reaction formula is presented in Scheme 2.

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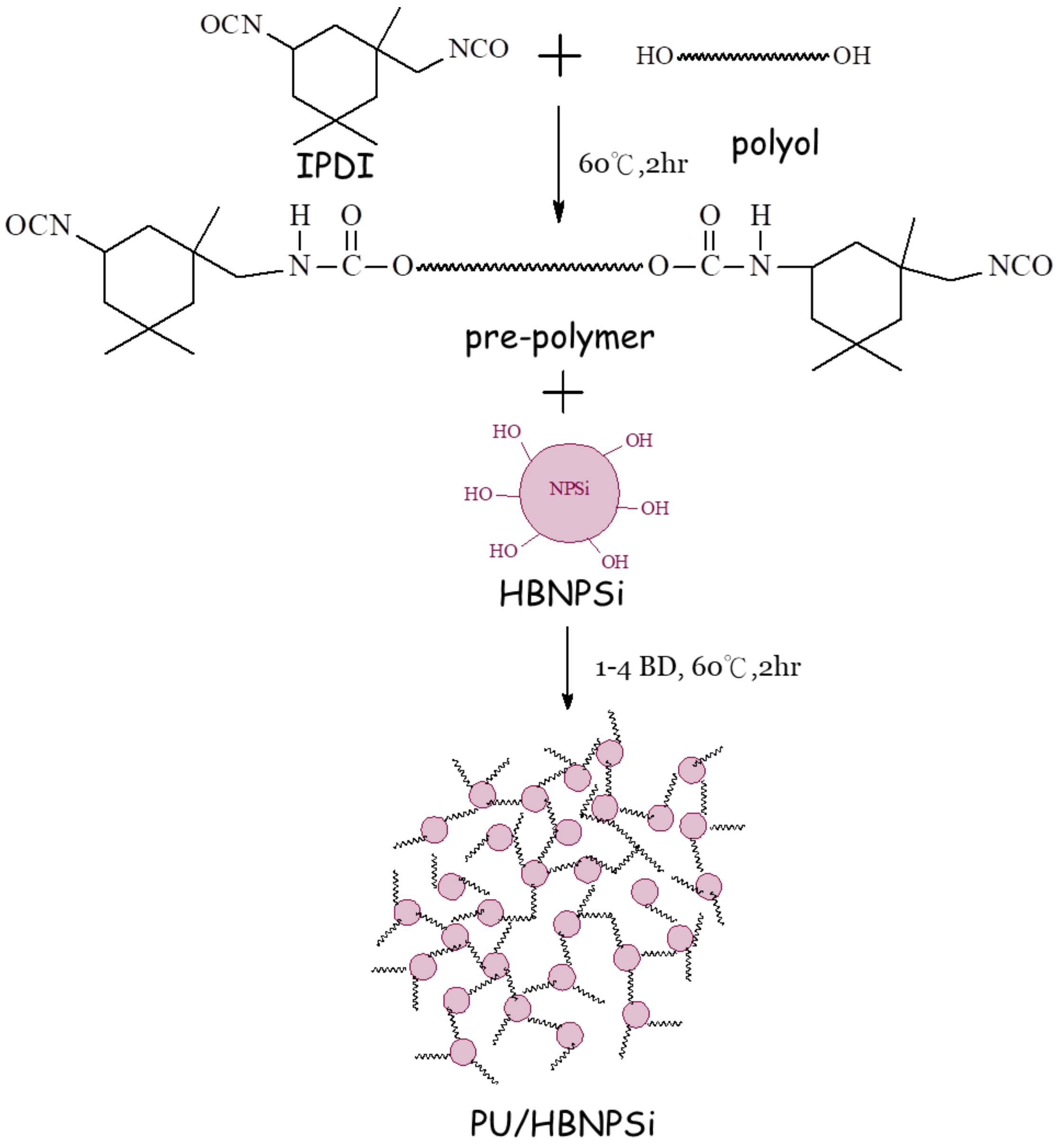

Scheme 2 the reaction of PU/HBNPSi.

2.4 Measurements

The FTIR spectra of the materials were recorded between 4000-400 cm^{-1} using a Nicolet Avatar 320 FT-IR spectrometer, from the U.S.A. UV/VIS spectra were tested on a Hitachi (Japan) U-3300 spectrophotometer and the sample was prepared as a thin film on a glass substrate by spin coating. Thin films were prepared by the solution-casting method. The samples were treated at 180℃ for 2hr and then ground into fine powder. The thermal degradation of composite was examined using a thermogravimetric analyzer (TGA) (Perkin Elmer TGA 7) from room temperature to 800 °C at a rate of 10 °C/min under an atmosphere of nitrogen. The measurements were made on 6-10mg samples.

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Weight-loss/temperature curves were plotted. The LOI is defined as the minimum fraction of O_2 in a mixture of O_2 and N_2 that will just support flaming combustion. The LOI test was performed according to the testing procedure of the ASTM D 2836 Oxygen Index Method, with a test specimen bar 7-15 cm long, 6.5 ± 0.5 mm wide, and 3.0 ± 0.5 mm thick. The sample bars were suspended vertically and ignited by a Bunsen burner. The flame was removed and the timer was started. The concentration of oxygen was increased if the flame on the specimen was extinguished before burning for 3 min or burning away 5 cm of the bar. The oxygen content was adjusted until the limiting concentration was determined.

3. Results and discussion

3.1 Characterization of PU/HBNPSi hybrid

The spectrum depicted in Fig. 1 exhibits the characteristic absorption peak of DOPO-BQ; the -OH functional group was between 3600 and 3200 cm^{-1} [9, 10], the P-Ph was at 1442 cm^{-1} [11], the P=O was at 1200 cm^{-1}, and the P-O-Ph was at 759 cm^{-1} [12]. This interacted with the -NCO functional group at 2270 cm^{-1} for the characteristic absorption peak of IPTS [13] and a ring opening reaction with the Oxirane ring functional group at 910 cm^{-1} for the characteristic absorption peak of TGIC [14, 15]. It was evident from HBNPSi that the -NCO functional group had already disappeared; the -NH functional group was between 3400 to 3300 cm^{-1} of -NH [16]; the C-N functional group was at 1471 cm^{-1} [12]; other characteristic absorption peaks of original DOPO-BQ, IPTS, and TGIC appeared. This proved that the reaction had successfully formed HBNPSi flame retardant.

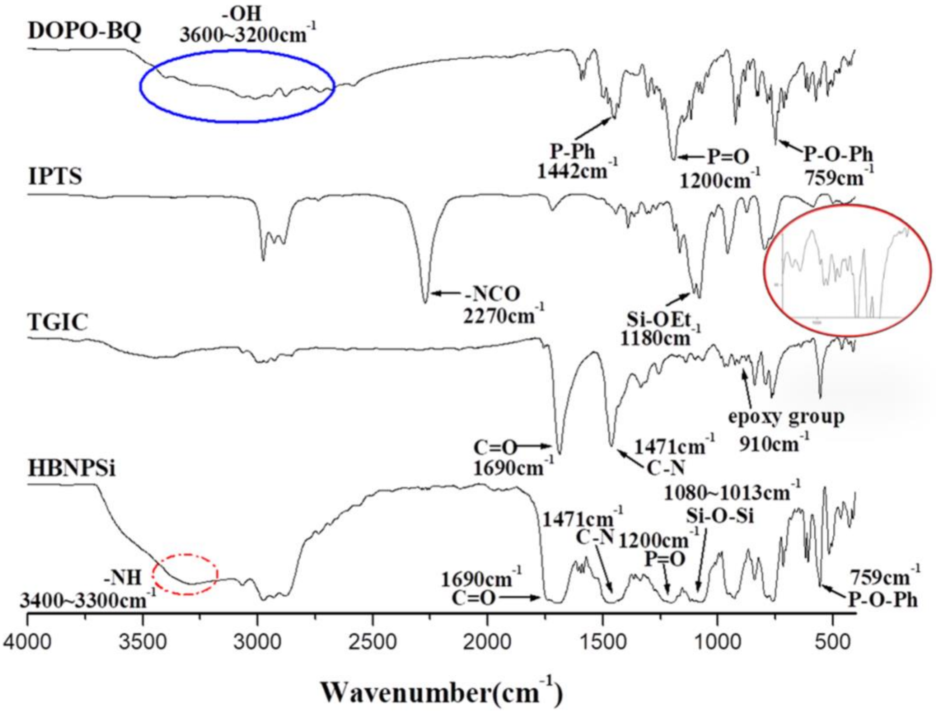

Fig. 1 FTIR spectra of DOPO-BQ, IPTS, TGIC and HBNPSi.

Fig. 2 explains a reaction of the -NCO functional group between 2270 cm^{-1} of prepolymer [13], with the -OH functional group between 3600 and 3200 cm^{-1} of HBNPSi [9, 10], and the -OH functional group with an added chain extender. The figure indicated that reaction of -NCO functional group of prepolymer had completed and had formed PU/HBNPSi. The original functional groups that appeared in Fig. 2 were –NH, C=O, C-N, P=O, P-O-Ph, and Si-O-Si, which verified that preparation of PU/HBNPSi hybrid material had been successful.

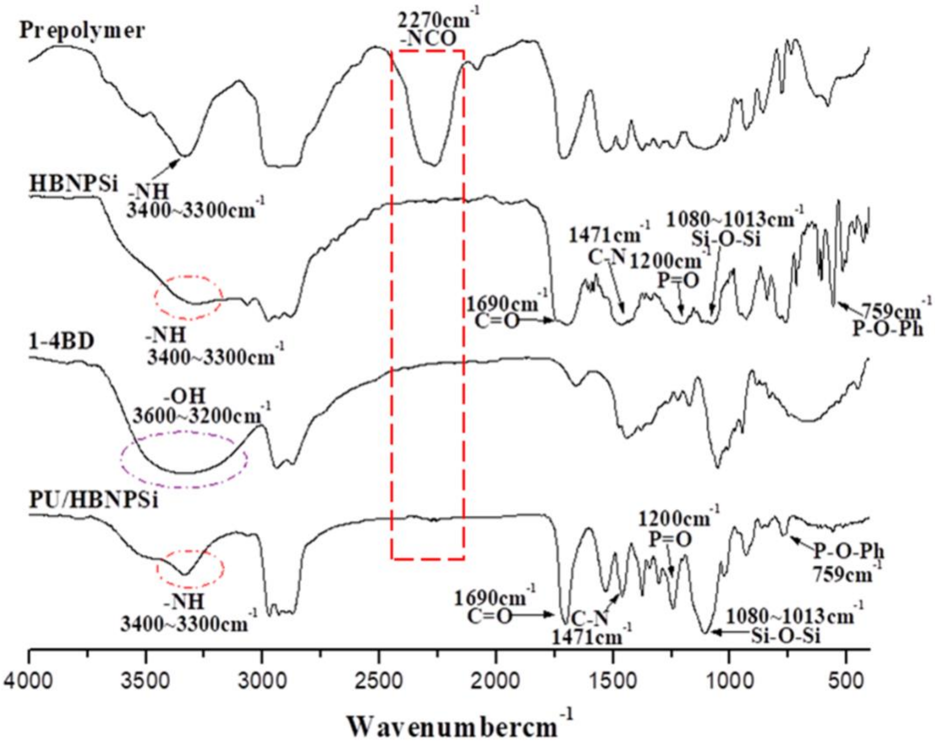

Fig. 2 FTIR spectra of Pre-polymer；HBNPSi；1-4BD and PU/HBNPSi.

3.2 Spectral transmittance analysis

The PU/HBNPSi hybrid material prepared through the sol-gel method in this study was subjected to UV/VIS testing in the visible range ($\lambda = 400$ to 800 nm) to determine its spectral transmittance.

Fig. 3 indicates that the UV/VIS spectra of various samples of PU/HBNPSi with different concentrations of HBNPSi had nearly 100% penetration within the visible range. This suggested that PU/HBNPSi hybrid material had excellent compatibility between organic phase and inorganic phase. Additionally, this indicated that flame retardant particles contained in the hybrid material were smaller than visible optical wavelength. The transparency of the material exhibited basic characteristics of nanomaterials, which has a wide range of applications.

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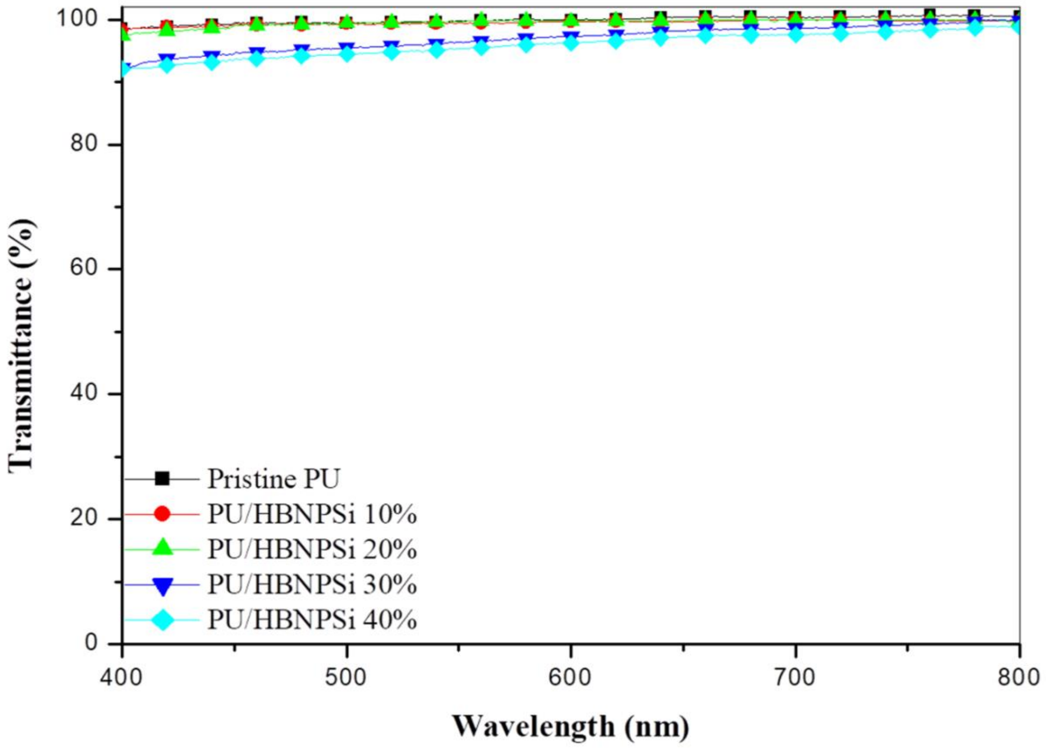

Fig. 3 UV/VIS Spectrum of Pristine PU and PU/HBNPSi hybrid.

3.3 Thermal property

The heating rate of TGA was set to 20 ℃/min and measurement was conducted under nitrogen environment. When various concentrations of HBNPSi flame retardant were mixed into PU samples, the changes were found in weight loss when the temperature was increased; the results are shown in Fig. 3, Fig. 4, and Table 1.

Changes in degradation curve can be observed from Fig. 4 and Table 1. The weakest C-NH chain of pristine PU caused degradation of hard segments of PU, which led to formation of isocyanates, -OH functional groups, -NH functional groups, and carbon dioxide [17]. The temperature was 302 ℃ when weight loss was 10% (T_{d10}). For PU samples with a high concentration of HBNPSi flame retardant, the T_{d10} of PU/HBNPSi 40% increased to 326 ℃. The char yield at 800 ℃ increased with an increase in the amount of HBNPSi added. Specifically, the char in pristine PU increased from 0.7 wt % to 8.1 wt %. This was because when HBNPSi underwent thermal degradation, its phosphorus tended to form a gas phase that captured free radicals, produced a condensed phase, and catalyzed the

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formation of char [18]. Additionally, due to surface migration phenomena [19, 20], silicon dioxide structures formed compact layer protected internal parts of the substrate. Benzene rings supplied the production of char and thus char layers had antioxidants that resisted high-temperature combustion. This indicated that adding HBNPSi increased thermal stability of the materials.

Fig. 5 presents a curve diagram of DTG for various changes in temperature. The temperature of maximum degradation rate of pristine PU was 343 ℃. The temperature of maximum degradation rate of PU/HBNPSi 40% increased to 376 ℃ in samples of PU with flame retardant. However, the maximum degradation rate of Pristine PU was −36 (wt %/min), but the value decreased to −17 (wt%/min) for samples with HBNPSi flame retardant. Flame retardant can effectively reduce the rate of thermal degradation in materials and produce slower material collapse. Thus, if flame retardants are used in the buildings and those buildings catch fire, the flame retardants increase the chance that residents and firefighters can escape from the burning building. Experimental evidence proved that adding HBNPSi flame retardant can effectively improve thermal stability.

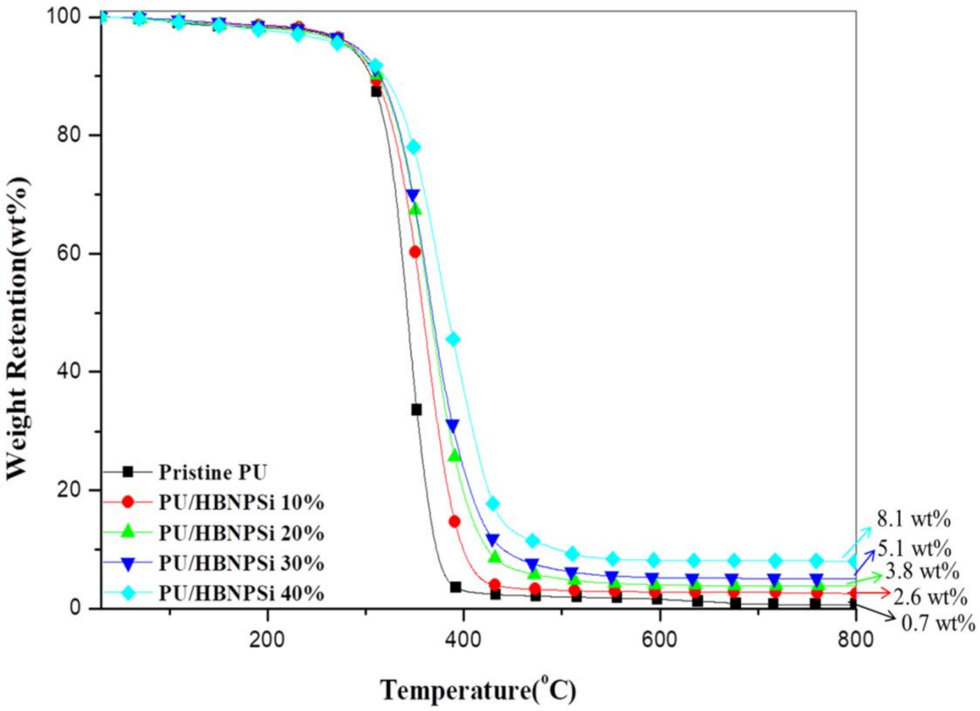

Fig. 4 TGA curves of PU/HBNPSi hybrid in N_2.

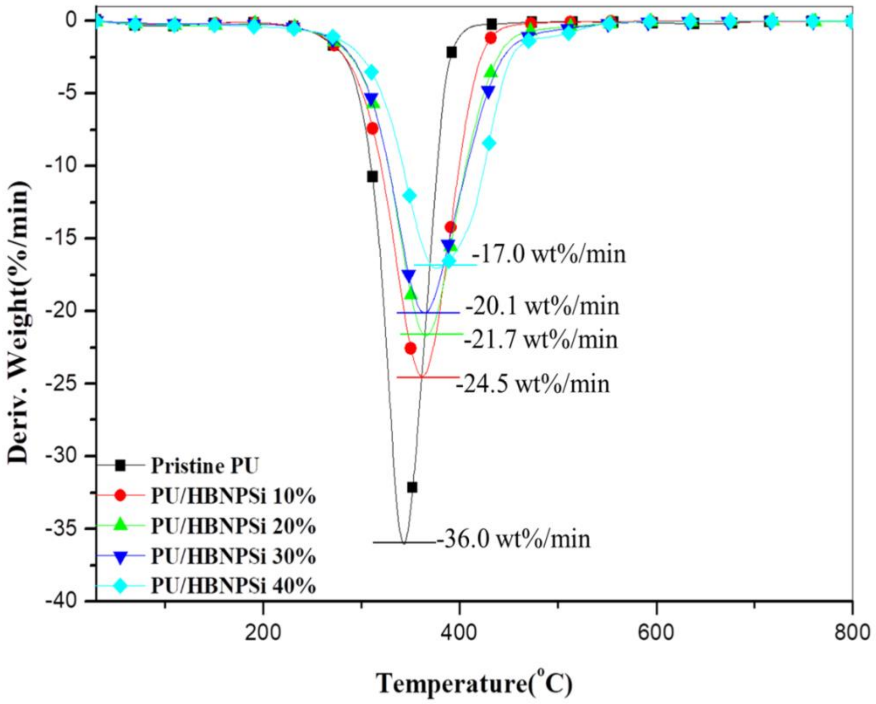

Fig. 5 DTG curves of PU/HBNPSi hybrid in N_2.

Table 1 Thermal properties of Pristine PU and PU/HBNPSi hybrid.

Sample NO.	$^{a}T_{d10}$(℃)	$^{b}T_{max}$(℃)	$^{c}R_{max}$(wt%/min)	IPDT(℃)	C.Y(wt%)
Pristine PU	302	343	-36.0	348	0.7
PU/HBNPSi 10%	306	361	-24.5	397	2.3
PU/HBNPSi 20%	308	365	-21.7	416	3.8
PU/HBNPSi 30%	311	365	-20.1	435	5.1
PU/HBNPSi 40%	326	376	-17.0	488	8.1

$^{a}T_{d10}$ is the temperature when the weight loss of sample reaches its 10%.

$^{b}T_{max}$ corresponds to the maximum temperature degradation rate.

$^{c}R_{max}$ corresponds to the maximum thermal degradation rate.

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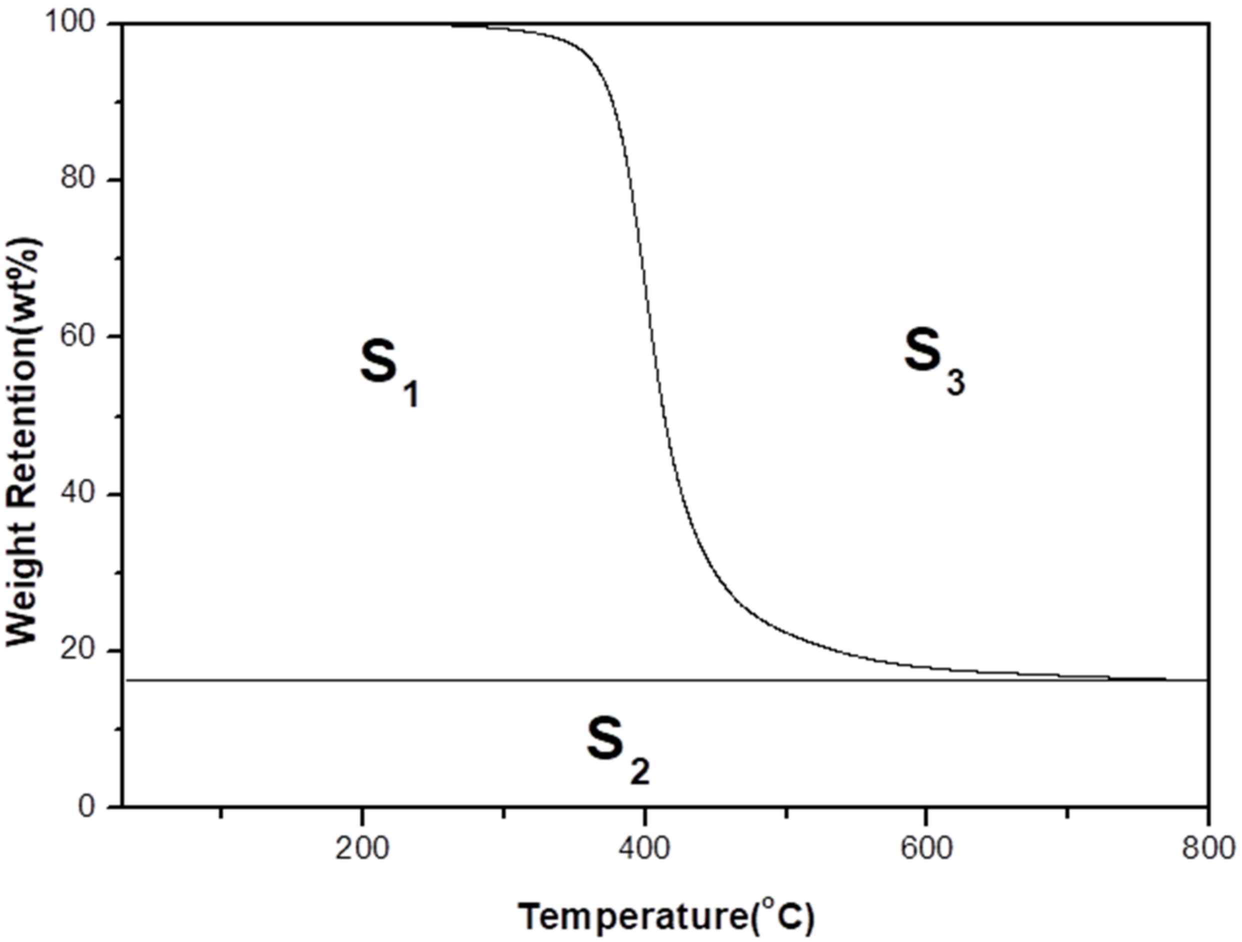
3.4 Integral procedural decomposition temperature (IPDT)

IPDT is a general method for evaluating the thermal stability of materials. A* denotes the ratio of the area of degradation curve derived from the overall experiment to the area of the overall TGA diagram, K* denotes the coefficient of A*, T_i denotes the initial temperature of the experiment, and T_f denotes the final temperature of the experiment. Two factors existed to influence IPDT value: (1) temperature of initial degradation and (2) char yield. A high IPDT value indicates a high thermal stability [21-23]; the calculation method is as follows: [24]:



The symbols' meanings are as follows:

IPDT(℃)= $A^* \times K^* \times (T_f - T_i) + T_i$

$A^* = (S_1 + S_2)/(S_1 + S_2 + S_3)$

$K^* = (S_1 + S_2)/S_1$

T_i=the initial experimental temperature

T_f=the final experimental temperature

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IPDT values were calculated by substituting the obtained values of T_i, T_f, S_1, S_2, and S_3 into the equation. IPDT values can be observed from Fig. 6 and Table 1. The IPDT value of pristine PU was 348 ℃. A sample with 40% HBNPSi flame retardant had an IPDT value of 488 ℃. The result verified that IPDT value increased with an increase in concentration of flame retardant and thermal stability increased up to 140%. This explained why HBNPSi can increase the thermal stability of PU hybrid materials. In this study, the key factors are excellent compatibility between organic and inorganic phases and compact structure, which contributed to the formation of char. Char layers contained silicon dioxide, which formed antioxidants that were resistant against high-temperature combustion. Thus, composite materials had superior thermal stability under high temperature.

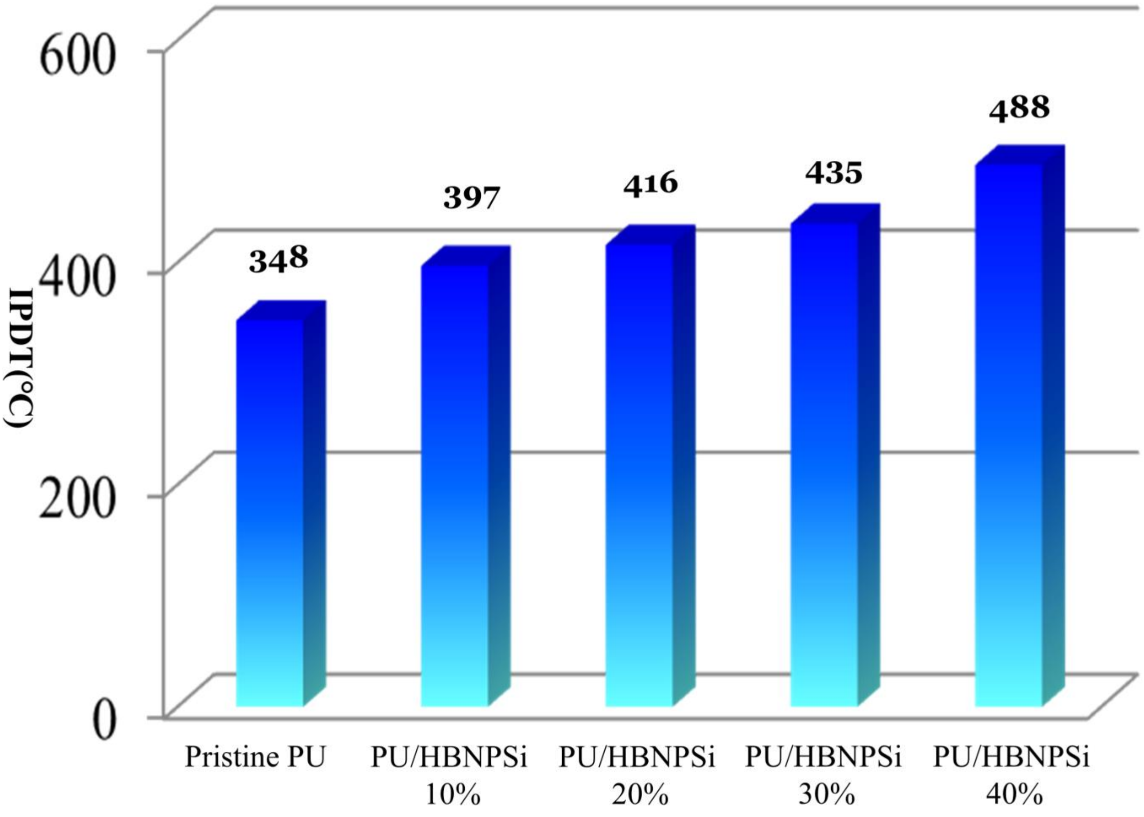

Fig. 6 The IPDT data of Pristine PU and PU/HBNPSi hybrid.

3.5 TGΔ

To investigate the synergistic effect of polymer materials in thermal degradation and combustion processes, TGΔ was calculated from the difference between weight losses of polymer matrix and composites [25, 26]:

$TG\Delta(wt\%)=M_{exp}-M_{the}$ ：curve of weight difference……(1)

where M_{exp} denotes the experimental value of TGA degradation in hybrid materials. M_{the} was calculated by using the substrate data and TGA degradation curves with different additive ratios. Fig. 7 showed that hybrid materials mostly had positive deviation and this indicated that an interaction effect existed between pristine PU and the HBNPSi additive. Additionally, it also revealed that compatibility between pristine PU and HBNPSi was excellent for improving the thermal stability and flame retardancy of composite materials.

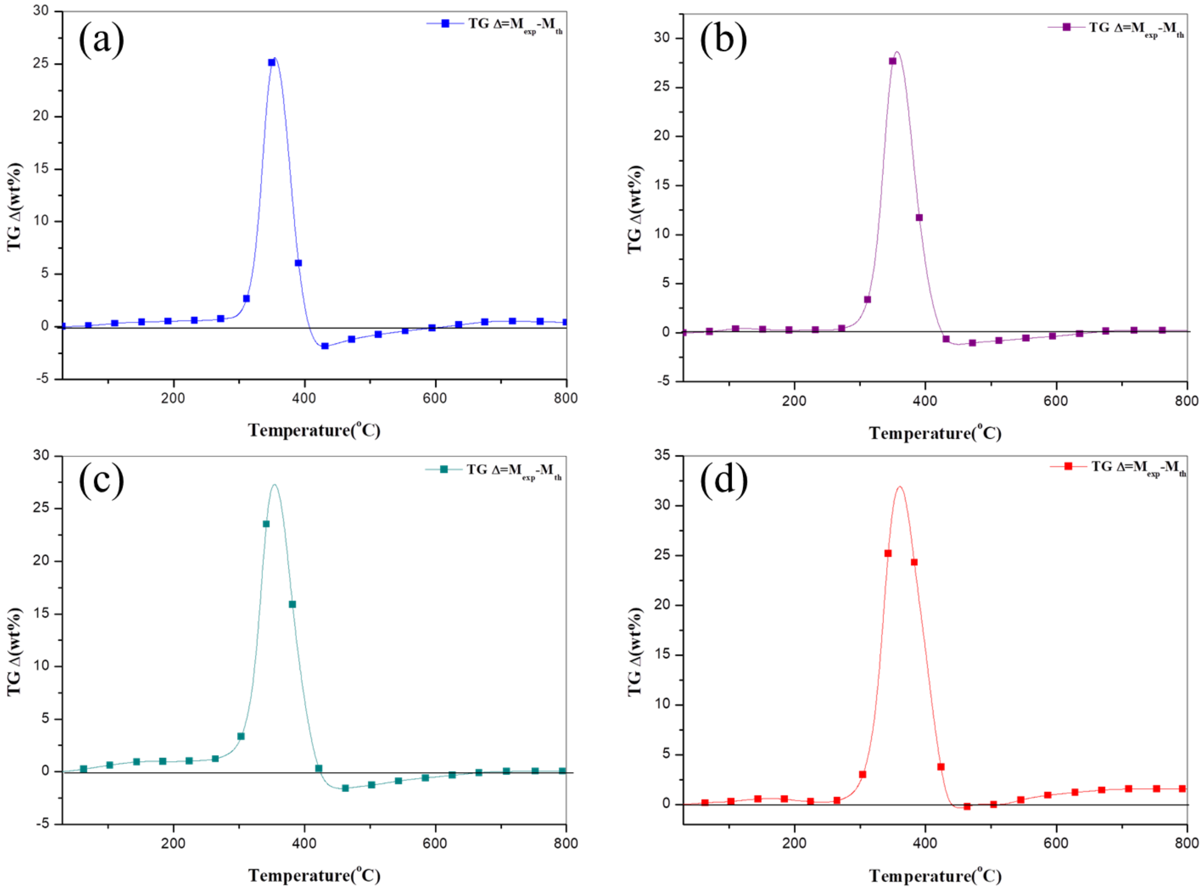

Fig. 7 Dependence of the interaction TGΔ on the degradation time for PU/HBNPSi (a)10% (b)20% (c) 30% (d) 40%.

3.6 Flame retardancy of the materials

LOI was used to judge the level of flame retradancy of polymer materials from differences in

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oxygen and nitrogen concentrations. Oxygen accounts for 21% of the atmosphere and when LOI is equivalent to 21 or below 21 the material burns freely, which are flammable. Materials with LOI values between 22 and 25 tend to be extinguished spontaneously during combustion. Materials with LOI values greater than or equal to 26 are considered difficult-to-ignite [27]; their adjusted flow rate settings of oxygen and nitrogen were measured (ml/sec) and the corresponding equation is as follows:

$$\mathrm{LOI} = \frac{O_2}{O_2 + N_2} \times 100$$

Fig. 8 and Table 2 show that pristine PU has an LOI index of 19 and thus can be designated as a highly flammable polymer material. When the flame retardant concentration increased to 40%, the LOI value of PU/HBNPSi hybrid material increased to 26 and flame retardancy increased by 7 levels. This demonstrated the excellent flame retardancy of HBNPSi flame retardant because in the process of thermal degradation, phosphorus in its structure tended to form a gas phase to capture free radicals, prevent the existence of a condensed phase, catalyze formation of char [18] and lead to surface migration phenomena of silicon [19, 20]. It also formed compact silicon dioxide structures that protected the internal parts of the matrix. Benzene rings supplied the production of char and thus char layers had antioxidant that resisted high-temperature combustion.

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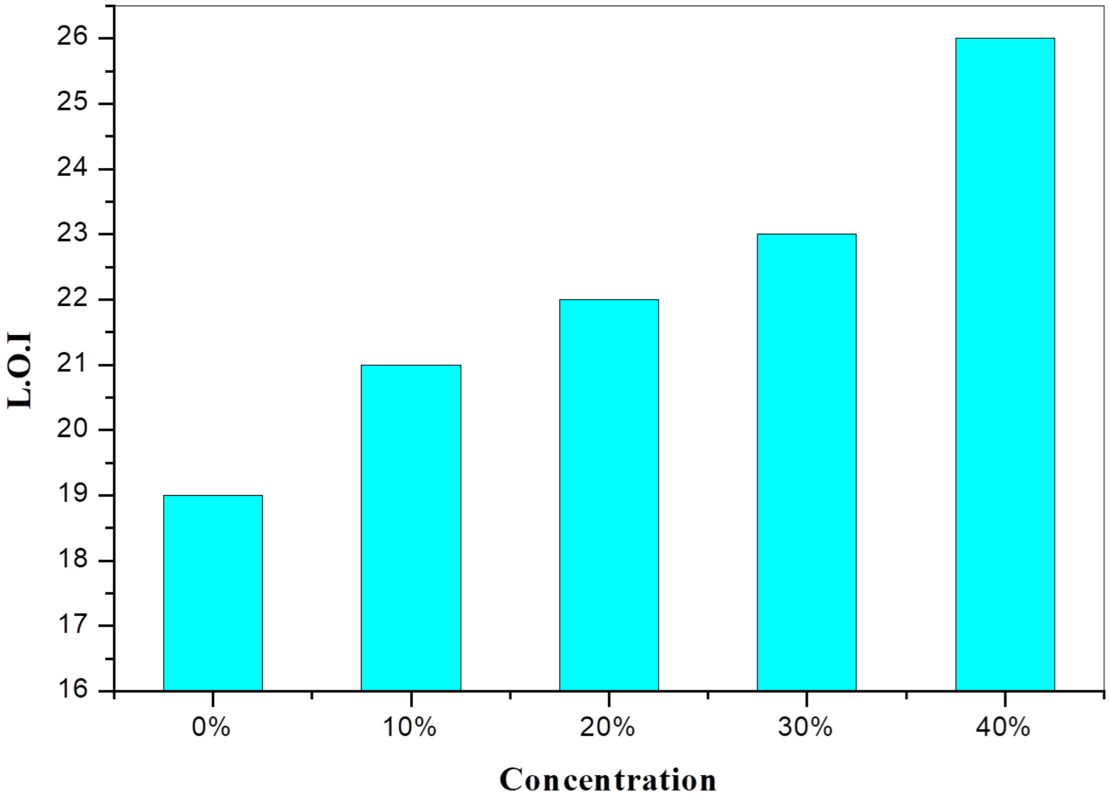

Fig. 8 Effect of various HBPSi contents on the LOI of PU/HBNPSi hybrid.

Table 2 The flame retardance of PU/HBNPSi hybrid by LOI values.

Sample	LOI	△LOI
Pristine PU	19	0
PU/HBNPSi 10%	21	2
PU/HBNPSi 20%	22	3
PU/HBNPSi 30%	23	4
PU/HBNPSi 40%	26	7

3.7 Char analysis by Raman analysis

Raman analysis was used to detect char obtained by placing PU/HBNPSi samples in an oven at 800 ℃ for either 1 minute or for 5 minutes. Additionally, it was used to observe changes in fluctuations of the D-band (Disordered band) and the G-band (Graphitic band) about carbon structure.

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The D-band was located at approximately 1350 cm^{-1} and was composed of carbon structures of irregular aliphatic compounds with sp^3 structure [28]; the G-band was located at 1580cm^{-1} and was composed of aromatic substances or the so-called carbon structures of six-membered rings; it had sp^2 graphite structure [29]. During combustion, the D-band was transformed to the G-band and the appropriate ratio can be obtained by dividing areas (D/G); that ratio can be used as an excellent indicator of carbonization level.

Fig. 9 and 10 indicated that changes in D-band and G-band among samples of PU/HBNPSi 10% and PU/HBNPSi 40% and results of analysis are shown in Table 3. The table showed ratios of 2.45 and 1.33 for PU/HBNPSi 10% following 1 minute and 5 minutes of combustion, respectively. When PU/HBNPSi samples contained 40% flame retardant, ratios of 0.66 and 0.40 were found following 1 minute and 5 minutes of combustion, respectively. A decrease in G/D ratio indicated that graphite accounted for the majority of char. A large amount of additives corresponded to a highly obvious carbonization effect. The melting point of graphite is higher than 3000 ℃; graphite is sufficient to withstand the temperature of a normal fire scene (normally at 800 °C). If an additive can effectively increase the char content of materials during combustion, the additive can improve the thermal stability and nonflammability of the materials.

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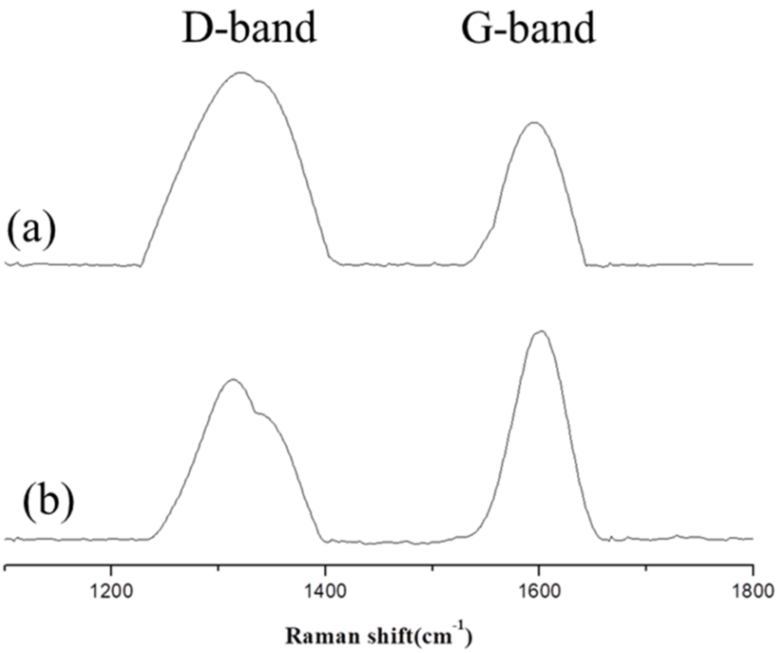

Fig. 9 The Raman spectra of char products from PU/HBNPSi 10% at 800 ℃ (a) 1 min (b) 5 min.

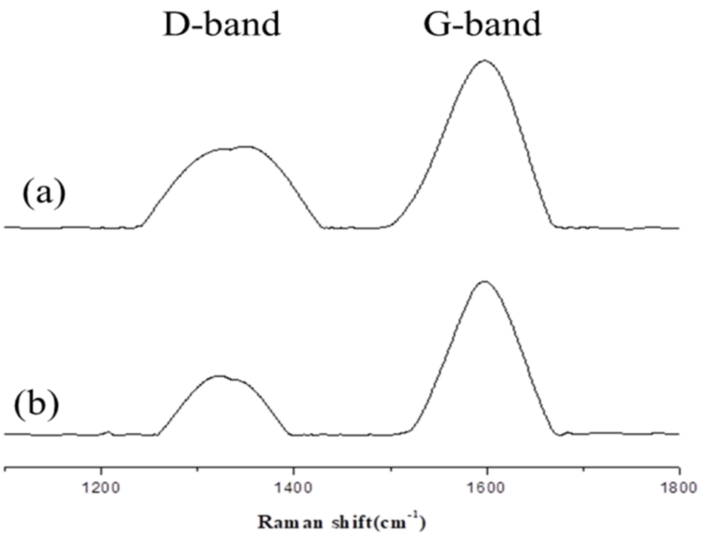

Fig. 10 The Raman spectra of char products from PU/HBNPSi 40% at 800 ℃ (a) 1 min (b) 5 min.

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Table 3 The area ratio of Raman shift from PU/HBNPSi hybrid char.

Sample NO.		D-band	G-band	D/G
		$1350cm^{-1}$	$1580cm^{-1}$	
PU/HBNPSi 10%	1min	31037	12662	2.45
	5min	26999	23826	1.33
PU/HBNPSi 40%	1min	19284	29133	0.66
	5min	15703	39396	0.40

4. Conclusion

FTIR was used to conduct structural characterization, to verify the successfully preparation PU/HBNPSi hybrid materials. Thermal properties were calculated through TGA curve diagrams. After HBNPSi flame retardant had been added, maximum degradation rate slowed down from −36 wt%/min to −17 wt%/min, the IPDT value increased from 348 ℃ to 488 ℃, and the char yield increased from 0.7 to 8.1 wt%. The aforementioned results showed that thermal stability of pristine PU improved after HBNPSi had been added. The LOI of pristine PU was only 19. For a sample of 40% flame retardant content, the LOI increased to 26; this proved that the sample was nonflammable. Raman char analysis of PU/HBNPSi hybrid materials determined the correlation between char formation and thermal properties. Raman spectra proved that the amount of char in PU samples increased as the amount of HBNPSi in the samples increased. After HBNPSi had been added, a sample's production of char during combustion increased markedly; this phenomenon became more obvious as concentration increased and thus the effects of increased thermal stability and flame retardancy.

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